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CZOCHRALSKI GROWTH OF $LaAlO_3$

FINAL REPORT

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I. SUMMARY

The objective of this program was to explore the possibility of growing high optical quality $LaAlO_3$ by the Czochralski method. The techniques developed for ruby growth were found to be directly translatable to $LaAlO_3$ with no apparent limitations imposed by the use of a crucible. Undoped and doped (Cr^{3+}, Eu^{3+}) crystals of various orientations were grown.

Two major defects were encountered: color centers and twinning. Color centers were eliminated by using high purity starting materials in combination with selected growth and post-growth treatment. Two mechanisms for forming color centers are proposed and their relation to $LaAlO_3$ defect chemistry is discussed. The dominant twin planes have been identified to be those of the (100) system. Their relation to the crystal structure of $LaAlO_3$ has been elucidated.

Isolated attempts were made to grow $BiAlO_3$ and $PrAlO_3$ to determine if twinning might be a problem in these potential host compositions; other growth problems were encountered indicating that an answer could be obtained only by an extensive effort beyond the bounds of the present program.

II. INTRODUCTION

Of the many known III-III perovskites (ABO_3), only one ($LaAlO_3$) has been found to exist in the ideal cubic phase; however, the cubic phase exists only at elevated temperatures. At room temperature, $LaAlO_3$ is rhombohedral, having a rhombohedral angle of 60°6' referring to the primitive rhombohedral cell or 90°5' referring to the face centered rhombohedral cell.

Because the departure of the unit cell from the cubic is so slight, it has been hoped that such a material would provide an attractive laser host for substitutional doping of trivalent ions in either the A or B sites. $LaAlO_3$ has been shown to be an attractive host in that fluorescence data from Cr^{3+} doped $LaAlO_3$ is reported to be

25[1] - 34[2] milliseconds at room temperature as compared to 3 milliseconds for Cr^{3+}: Al_2O_3, while for Nd^{3+} doped $LaAlO_3$, the lifetime of the dopant is enhanced by a factor of two relative to that in $CaWO_4$ and Y_2O_3[2].

However, $LaAlO_3$ heretofore available was unattractive optically because of a twinning defect. The material on which fluorescence data were obtained was Verneuil grown. The present work was undertaken to explore whether Czochralski-grown material suffered the same defect or whether, by virtue of reduced stresses during growth, twinning would be avoided. In the course of this program it became apparent that the structural basis for twinning needed elucidation. Hence this aspect of the problem received attention.

III. CRYSTALLOGRAPHIC DATA

A. Structure

Geller and Bala[3] have done an extensive survey of rare-earth aluminates and in particular $LaAlO_3$. They reported that $LaAlO_3$ is rhombohedral belonging to the space group $R\bar{3}m$ and having unit cell dimensions of a = 5.357Å $\alpha = 60°6'$ at room temperature. The above symbols mean that the unit cell has a 3 fold inversion axis along the body diagonal and a mirror plane parallel to this axis as symmetry elements.

The Al^{3+} occupy the eight corners of the rhombohedron and its center (Figure 1). In addition to being on the 3 fold axis, they occupy the inversion center of the unit cell. The La^{3+}, however, do not occupy an inversion center, but are approximately 0.01Å from it along the body diagonal, as indicated by arrows in Figure 1.

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1) F. Forrat, R. Jansen and P. Trevoux, Comptes Rendus Acad. Sci. t 256 1271 (1963).

2) Laser Materials Final Report - Korad Corporation No. AD 439901.

3) S. Geller and V. B. Bala, Acta Cryst., 9 1019 (1956).

Derighetti, et al.[4], however, report the most probable space group to be $R\bar{3}c$ on the basis of electron paramagnetic measurements. In this space group, the mirror plane is replaced by a glide plane; however, the Al^{3+} positions remain the same as in $R\bar{3}m$. The structure would thus have equivalent La^{3+} sites and Al^{3+} sites. In either space group, the Al^{3+} are the only atoms located on an inversion center and long fluorescence lifetimes can only be predicted for atoms substituted on the B site. This, in fact, seems to be the case for Cr^{3+} and not for rare-earth dopants on the A site.

B. Phase Change

In addition to the room temperature data on $LaAlO_3$, Geller and Bala took high temperature x-ray powder patterns of $LaAlO_3$. Here they found a gradual change from the rhombohedral to the cubic cell with increasing temperature. They were unable to detect any additional change above 350°C. Wood[1], however, observed a phase change at 435°C ± 25°C. DTA showed no indication of a phase change implying that there is no appreciable heat of transition. Such results would probably indicate a second order transition.

Visible observations of the phase change of crystals from 1/2-inch to 2-inches in length in the present work showed it to be a gradual change as reported by Geller and Bala; however, the rhombohedral phase could be seen up to 512°C ± 3°C. This value is 77°C above that of Geller and Bala, 65°C above that reported by Gränecker and Müller[5] and 22°C above that reported by Bondar and Vinogradova[6].

C. Density

The theoretical x-ray density for $LaAlO_3$ using the cell constants as reported by Geller and Bala was calculated in this work to be 6.51 g/cc while the

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4) B. Derighetti, J.E. Drumheller, F. Laves, K. A. Müller and F. Waldner, Acta Cryst. 18 557 (1965).

5) H. Gränicher and K. A. Müller, Nuova Cim., Suppl. 6 Serx. X 1216 (1957).

6) I. A. Bondar and N. V. Vinogradova, Izr. Akad. Nauk. SSSR, Ser. Khim. 5 785 (1964).

measured density of the solid crystal boules was found to be 6.16 g/cc. This agreement confirms the doubly primitive (two molecules per unit cell) rhombohedral unit cell chosen by Geller and Bala. Bondar and Vinogradova report a density of 5.84 g/cc, probably applying to powder samples.

IV. EXPERIMENTAL

A. Crystal Growth

The crystal growth chamber used for pulling ruby was found to be directly applicable to $LaAlO_3$ without change of design or materials. The chamber provides for atmosphere control (neutral or H_2-containing atmospheres were used for $LaAlO_3$ growth) and temperature control. The crucible was charged with La_2O_3 powder and crystalline Al_2O_3 (Verneuil crackle) in stoichiometric ratio. The melting point of pure $LaAlO_3$ was read to be 2075-2080°C, uncorrected pyrometer values. Several melts were checked for stoichiometry after having been held for 6-8 hours above the melting point and were found to have maintained stoichiometry with no detectable departure therefrom. There was no visible attack of the crucible and no crucible contaminant was found in the frozen melt by emission spectroscopy.

Crystals ranging from 8.5 to 43 grams and from 1/2-inch to 4-inch length were grown. A total of five different boule axis orientations were obtained; referred to the pseudo-cubic unit cell (transformations from cubic to rhombohedral to hexagonal indices are given in Appendix I) these were as follows: ⟨111⟩, 20° from ⟨111⟩, ⟨$2\bar{1}\bar{1}$⟩, 10° from ⟨$2\bar{1}\bar{1}$⟩, and ⟨$3\bar{1}\bar{1}$⟩.

Several doped crystals were pulled in the "10° from ⟨$2\bar{1}\bar{1}$⟩" orientation. Two different dopants were used separately: Cr^{3+} as a B site dopant and Eu^{3+} as an A site dopant, each introduced into the original charge as the sesquioxide. The melting point of the Cr-doped charge was higher than that of pure $LaAlO_3$ and increased with the Cr concentration in the range .07-2.2 wt % Cr_2O_3. The Eu-doped charge (0.1 to 1 wt % Eu_2O_3) did not show a melting point differen relative to pure $LaAlO_3$.

The La_2O_3 used initially for growth of $LaAlO_3$ was obtained from American Potash and had a purity rating of 99.99 and 99.997% with respect to rare earths (Code 528 and 529 respectively). Calcium, magnesium and silicon impurities were found to be present in concentrations of from 100 to 200 ppm each. All crystals grown from this material were a dark yellow-brown in color. At the present time a special grade of La_2O_3 has been obtained which has a total non-rare earth impurity level of about 60 ppm, the majority of this being silicon while the calcium and magnesium total less than 15 ppm. Crystals grown with this material are clear and colorless.

It was noted that during the initial heating of the unreacted oxides, two characteristic "breaks" could be seen in the heating curve. The first break occurred at about 1650° to 1660°C and was accompanied by a complete change in the character of the charge. The material would "puff" to perhaps twice its original volume. At about 1715°C, the exact reverse would occur, i.e., the "puffed" material would collapse into a dense charge and thereafter no change was noted until the melting point was reached.

The "puffed" material was very plastic at that temperature and it is believed the "puffing" is a result of a solid-solid reaction between the oxide components of the charge. The collapse of the charge is believed due to the increase in plasticity of the material with increasing temperature.

B. Crystal Quality

During the course of the first few tests, it became apparent that the seed orientation strongly affected the overall quality of the crystal. In the first few crystals pulled, a central defect could be seen which usually ran the length of the crystal. This defect was then terminated at the growth interface by a small depression. Figure 2 shows a photograph of such a depression. Examination of the figure will show that the depression is composed of many facets giving it an overall appearance of hopper growth. These facets have been found to be the (100) faces of the pseudo-cubic unit cell. It is believed that the central defect is a

result of an overgrowth of the "hopper" section of the growth interface.

Such defects as described above have been found on all undoped crystals of $LaAlO_3$ that were grown along a low index direction. The crystals which have been grown along a high index direction did not show this defect and had few, if any, bubbles. Such results as described above would suggest that growth along a high index direction is desirable.

Another factor which strongly affected the crystal quality was the type of dopant used. When Cr^{3+} was placed in the melt, two things became apparent. First, as mentioned before, the melting point of the material was raised and more important the crystal quality of the boule dropped considerably. The addition of Cr^{3+} to the melt enhanced the faceting tendency of $LaAlO_3$ to such an extent that the (100) face was formed on the growth interface even though growth was in a high index direction. This faceting again led to the formation of oriented voids and bubbles throughout the entire crystal. A photograph of the growth interface of a Cr^{3+} doped crystal is shown in Figure 3.

One approach which can be taken is to grow at much slower rates. Several attempts at slow growth rates yielded promising results and crystals of Cr^{3+} doped $LaAlO_3$ have been grown with only a few bubbles and voids; however, examination of these crystals still showed twinning to about the same extent as in the undoped crystals.

Doping on the "A" site is an entirely different matter. Good quality Eu^{3+} doped crystals of $LaAlO_3$ have been pulled with no evidence of facets as were seen in the Cr^{3+} doped samples, though both were grown off the same seed rod. Examination of ionic sizes of Eu^{3+} and Cr^{3+} as compared to La^{3+} and Al^{3+} respectively shows a much better "fit" for Eu^{3+} than for Cr^{3+}. This fit could be part of the reason for the ease at which Eu^{3+} doped $LaAlO_3$ can be grown.

A third parameter which strongly affects crystal quality is the pulling rate. Crystals of undoped $LaAlO_3$ have been pulled at rates from 1/16 to 1 1/2-inches per hour. The crystals pulled at a rate of greater than 0.60-inches per hour showed

a slight lineage structure in the center and as the pulling rate was increased so did the lineage increase until a point was reached where the entire crystal becomes opaque due to lineage. Figure 4 shows the effect of pulling rate on crystal quality.

C. Crystal Defects in $LaAlO_3$

Two defects exist in $LaAlO_3$ which would be detrimental to its use as a laser host. These defects are color centers and twinning. Both of these must be eliminated before single crystals of $LaAlO_3$ can be used for a laser host material.

1. Color Centers

The first of these defects which must be eliminated are color centers which give the crystal a yellow-brown color. Forrat, Jansen and Trévoux[1] report that these color centers are due to vacancies on the La^{3+} site and can be removed by substituting on the vacant site mono-, bi-, or trivalent ions. Furthermore, they state that these are V color centers which implies a positive ion vacancy-hole combination. In addition to the La^{3+} ion vacancy, it has been found that the purity of the starting materials strongly affects the color of the final boule. As has been found in other crystal growth problems, e. g., Al_2O_3 and YAG, the presence of alkaline earths such as calcium or magnesium greatly affects crystal clarity.

The problem then becomes one of (1) eliminating the impurity atoms which cause the discoloration of the crystal or (2) permanent "bleaching" of the color from the crystal. Of the two choices, the first is by far the best. As already mentioned above, the first objective has been accomplished by use of a special grade La_2O_3.

"Bleaching" of the color from the boules has also been accomplished by growth in a hydrogen atmosphere or by heating the boules under vacuum to 1800°C for about 1 1/2 hours. The vacuum heated crystals, when removed, from the furnace were colorless; however, exposure to UV light caused them to again return to their original color.

The hydrogen "bleached" crystals were colorless as grown; however, as in the vacuum heated case, UV light caused them to turn to the characteristic yellow-brown color. Unlike the vacuum heated crystals, however, the color was not permanent and the crystals gradually became colorless after several hours. It was also found that prolonged heating in air at 450°C caused both the vacuum heated and hydrogen "bleached" to become permanently discolored. It should be pointed out that these dark crystals were grown from Code 528 or 529 La_2O_3.

2. Twinning

The other major defect in $LaAlO_3$ is twinning of the crystals which is a direct result of the phase change from the ideal, cubic perovskite structure to the rhombohedral structure. This phase change is accompanied by a gradual shift of the La^{3+} ion along the body diagonal of the pseudo-cubic unit cell and a shift in the opposite direction of the adjacent "body diagonal" La^{3+} ion. Such shifts as described above are accompanied by a distortion of the cubic cell. The rhombohedral-cubic-transformation and the direction of the La^{3+} ion shift are shown in Figure 1. The twins result when the initial shift of the La^{3+} ions at various parts of the crystal are along different, equivalent cube body diagonals. It should be pointed out that the twins formed have identical structures and the only difference lies in the orientation of one part of the crystal with respect to another part.

To determine the sets of twins present, disks of three different orientations were cut from a boule: (100), (110), (111), these indices defining the planes parallel to the disk surface. The (100) disk, shown in Figure 5b, showed two distinct sets of twin planes. These sets are at right angles to each other and are perpendicular to the disk surface. The (110) disk, shown in Figure 5a, showed two sets of twin planes. One set is perpendicular to the disk surface while the other set is inclined from the surface. A difference in the extinction angle between the two parts of the crystal separated by the perpendicular twin plane was found to be 30 ± 10 arc minutes. Figure 5c shows the (111) disk which has three separate sets of twin planes present. All these sets are inclined with respect to the disk surface, i.e. (111) plane.

Several attempts have been made to remove the twinning by annealing. Although heat treatment does not remove the twinning, it does tend to produce large areas where only one direction of twin planes are present and reduce the twinning to some extent.

D. Spectroscopy of Doped Samples

The fluorescent spectra of both the Cr^{3+} and Eu^{3+} doped samples of $LaAlO_3$ were taken using an ARL Quantograph and agreed closely with that reported by Korad Corporation. The Cr^{3+} doped sample of $LaAlO_3$ showed a line at 7350Å and had a line width of approximately 8Å at room temperature. No low temperature data was taken nor were lifetimes measured.

The Eu^{3+} doped sample showed four strong lines which are: 4462Å, 5175Å, 5930Å and 6175Å; however no line widths were measured. As in the case of the Cr^{3+} sample, no low temperature data was taken nor lifetimes measured.

E. Growth of Related Hosts

1. $BiAlO_3$

At the start of this program, a search of the literature revealed numerous references to rare-earth aluminates. It was found that all these were of rhombohedral or lower symmetry, but as the rare-earth ionic radius increased, the material tended toward the cubic phase as shown in Figure 6 which shows the pseudo-cubic angle as a function of the "A" ionic radius.

If the curve can be extrapolated, an ionic radius of 1.20Å of a 3 plus ion could yield a cubic III - III perovskite at room temperature. Such an ion is Bi^{3+} which is reported to have an ionic radius of 1.20 in some literature. Furthermore a reference [7] was found in which $BiAlO_3$ was reported. With these facts in mind, an attempt was made to form $BiAlO_3$.

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7) Naray-Szabo, Publ. Univ. Tech. Sc. Budapest 1 30 (1947).

One to one mole ratios of Bi_2O_3 and Al_2O_3 were mixed together and heated in a platinum crucible for 1 to 5 hours and at temperatures of from 800 to 1200°C. Examination of the frozen melt did show small hexagonal crystals, however, these were found to be α - Al_2O_3 only. Further attempts to produce $BiAlO_3$ gave only the α - Al_2O_3 crystals.

2. $PrAlO_3$

$PrAlO_3$ is reported to have the same space group as $LaAlO_3$; however, the distortion from the cubic is slightly more, the rhombohedral angle being 90°17' as compared to arc 90°5' for $LaAlO_3$[1]. The symmetry of the Al^{3+} site remains the same as in $LaAlO_3$, and therefore Cr^{3+} doped $PrAlO_3$ should exhibit the same fluorescence characteristics as Cr^{3+} doped $LaAlO_3$.

Furthermore, it was reported that the rhombohedral angle at 950°C was 90°9'[1]. It was thought that a way to avoid the twinning problem in $LaAlO_3$ was to grow Cr^{3+} doped $PrAlO_3$ if the material melted while still in the rhombohedral phase. This value would be about 1950°C. The melting point of $PrAlO_3$ was found to be 2050°C or very close to the melting point of $LaAlO_3$. The material was much harder to grow than $LaAlO_3$ and had an emerald green color whose origin was not identified. The sample that was pulled was of insufficient optical quality to determine if twinning was present or not. Because of the difficulty of growth, no additional attempts were made to grow $PrAlO_3$.

V. DISCUSSION

A. Color Centers

As stated before, it was found that the problem of color centers in $LaAlO_3$ can be linked directly to the non-rare earth impurities in the starting material, in other words, the higher the non-rare earth impurity concentration, the more color centers produced. As a result of this observation, the color center problem in $LaAlO_3$ can be eliminated by careful selection of the starting material, giving particular attention to the concentration of calcium, magnesium and silicon.

If an alkaline earth impurity, either calcium or magnesium, is chosen as the color center producing agent, two possible mechanisms can be formulated to explain the experimental results. The first proposed mechanism consists of the diffusion of hydrogen into the crystal lattice and the association of the hydrogen with the lattice defect (color center). This mechanism is very similar to that proposed by Forrat, Jansen and Trévoux and can be represented by the following equations using the nomenclature of Kröger and Vink[8].

$$H_2 \rightleftarrows 2H_i \qquad (i = \text{interstitial}) \tag{1}$$

$$H_i \rightleftarrows (H_i^+)^{\cdot} + e^- \tag{2}$$

$$(Ca^{3+}_{La^{3+}}) \rightleftarrows (Ca^{2+}_{La^{3+}})' + e^+ \rightleftarrows V \text{ color center} \tag{3}$$

$$(Ca^{2+}_{La^{3+}})' + (H_i^+)^{\cdot} \rightleftarrows (Ca^{2+}_{La^{3+}}\ H_i^+)^{\circ} \tag{4}$$

$$e^+ + e^- \rightleftarrows \text{ground state} \tag{5}$$

If such a mechanism existed, heating a "hydrogen containing crystal" would tend to drive off the hydrogen and produce color centers. Likewise, exposure to UV light could supply enough energy to break up the complex formed in equation (4); however, in this case, the hydrogen would be retained and could again complex with the calcium defect. This mechanism does not explain the disappearance of the color centers when heated in a vacuum. In fact, one would predict on the basis of the above mechanism an increase in the number of color centers in the crystal due to the evolution of hydrogen under vacuum.

The second mechanism results in the formation of oxygen vacancies due to the reduction of the oxygen partial pressure by the hydrogen. These vacancies would then tend to produce electrons in a similar manner as did the hydrogen. The increase in the concentration of the electrons would tend to reduce the hole concentration and therefore the color center concentration. This mechanism can be represented as follows:

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8) F. A. Kröger and H. J. Vink, Solid State Physics 3 307 (1956).

$$(V_{O^{2-}}^{2-})^{\circ} \rightleftarrows (V_{O^{2-}})^{\cdot\cdot} + 2e^{-} \qquad (V = \text{vacancy}) \tag{6}$$

$$(Ca_{La^{3+}}^{3+}) \rightleftarrows (Ca_{La^{3+}}^{2+})' + e^{+} \rightleftarrows \text{V color center} \tag{7}$$

$$e^{+} + e^{-} \rightleftarrows \text{ground state} \tag{8}$$

In a neutral atmosphere, the following equilibrium can be thought to exist between the solid and gas:

$$(La^{3+})_{1-2\delta} (Ca_{La^{3+}}^{2+})'_{2\delta} (Al^{3+}) (O^{-2}) + 2\delta e^{+} \rightleftarrows$$

$$(La^{3+})_{1-2\delta} (Ca_{La^{3+}}^{2+})'_{2\delta} (Al^{3+}) (O^{-2})_{3-\delta} (V_{O^{-2}})^{\cdot\cdot}_{\delta} + \frac{\delta}{2} O_2 (g) \tag{9}$$

Any reduction of the equilibrium oxygen vapor pressure in the atmosphere would tend to drive the above reaction to the right producing more oxygen vacancies in the lattice. Such a reduction can be accomplished by either vacuum heating or growth in a reducing (hydrogen) atmosphere. If such a sample were heated in air, a decrease in oxygen vacancies would result with a corresponding increase in the number of holes.

Of the two mechanisms proposed, the second appears more likely than the first since identical results can be accomplished by the use of CO as reported by Forrat et al. [1] Also the second mechanism appears more probable when compared to other perovskites such as $SrTiO_3$ which are known to have an oxygen vacancy-oxygen partial pressure equilibrium.

B. Twinning

The other major defect found in $LaAlO_3$ which greatly affected the optical properties of the boules was the twinning which resulted from the phase

transformation from cubic to rhombohedral. Buerger[9, 10] has shown that crystals connected by a high-low phase transformation possess related symmetries, i.e. the symmetry of the low temperature form is a subgroup of the symmetry of the high temperature form. This implies that the symmetry of one form can be derived from that of another form by the suppression of one or more symmetry element sets in the unit cell. Furthermore, derivative structure theory can provide a basis for the prediction of the twin boundaries formed by such a phase transition and the prediction that the suppressed symmetry element can become the symmetry element of the twin.

For the case of $LaAlO_3$, the high temperature form is the cubic perovskite form which belongs to the point group m3m, space group Pm3m, while the low temperature (rhombohedral) form belongs to the point group $\bar{3}$m and either the space group R$\bar{3}$m or R$\bar{3}$c. The International Tables for x-ray Crystallography, Vol. I[11] shows that the point group $\bar{3}$m is a subgroup of the point group m3m and likewise for the space group. Thus the suppressed symmetry set which results from the phase transformation is the set of mirror planes (m) perpendicular to the cube axes. The mirror planes perpendicular to the face diagonals remain as does the three fold axis. An inversion three fold axis arises due to the doubling of the original cubic unit cell to form the rhombohedral cell. Therefore, one would predict the twin planes to be mirror planes (as are most twin planes) perpendicular to the ⟨100⟩, ⟨010⟩ and ⟨001⟩ directions of the original cubic unit cell. Such twins are referred to as transformation twins and result in a change of direction (approximately 70°) of the ⟨111⟩ axis (body diagonal) of the true rhombohedral cell at the twin boundary. These predictions on the twin boundaries agree with the results observed on the (100) disk, the (110) disk and the (111) disk as shown in Figure 5.

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9) M. J. Buerger, Am. Min. 30 469 (1945).

10) M. J. Buerger, J. Chem. Phys. 15 1 (1947).

11) International Tables for X-Ray Crystallography, Vol. I p 36 (1952).

Two other forms of twins could exist. One of these forms occurs along the face diagonals of the cube that are not in the same plane as the body diagonal. However, such a twin requires the La^{3+} ions on the twin plane (mirror plane placed in the (110) plane) to occupy a special position on the twin plane. This form of twinning is more disruptive to the crystal than the transformation twin since it does require the La^{3+} ions to occupy their "cubic positions" on the twin plane. Since such a position would be highly unstable, the La^{3+} ion would tend to "flip" to one of the other rhombohedral directions and form a (100) twin.

The third form of twinning which might occur is along the (111) face of the cubic unit cell or the faces of the rhombohedral unit cell. This form of twin represents a gross distortion from the original cubic phase and can not be formed by a simple change of direction of the La^{3+} ion shift and therefore can only be formed during growth of the crystal. Such a twin is called a growth twin and is shown in Figure 7 along with the other forms of twinning discussed.

Of the three forms of twinning possible, only the transformation twin has been found in the crystals grown.

APPENDIX

I. CUBIC-RHOMBOHEDRAL-HEXAGONAL TRANSFORMATION

Because the departure of the rhombohedral unit cell is so slight when compared to the cubic cell, it is easier to refer different crystal directions to the cubic cell. The following matrix represents the transformation from the cubic to the rhombohedral unit cell. It should be stated that this transformation applies only for a rhombohedral angle of between 59 and 61°.

Transformation matrix

$$\begin{pmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix}$$

or

Transformation equations

$$h_R = h_C + \ell_C$$
$$k_R = h_C + k_C$$
$$\ell_R = k_C + \ell_C$$

where h, k, and ℓ refer to the Miller indices while C and R refer to the cubic and rhombohedral phases respectively. The inverse of the above matrix is:

$$\begin{pmatrix} 1/2 & 1/2 & -1/2 \\ -1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \end{pmatrix}$$

or

$$h_C = 1/2\,(h_R + k_R - \ell_R)$$
$$k_C = -1/2\,(h_R - k_R - \ell_R)$$
$$\ell_C = 1/2\,(h_R - k_R + \ell_R)$$

Likewise a similar transformation exists for a rhombohedral to hexagonal unit cell relationship. Unlike the cubic-rhombohedral transformation, this applies to any hexagonal or rhombohedral system. The hexagonal-rhombohedral transformation matrix is given as follows:

$$\begin{pmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{pmatrix}$$

or

$$h_H = h_R - k_R$$
$$k_H = k_R - \ell_R$$
$$\ell_H = h_R + k_R + \ell_R$$

where H refers to the hexagonal unit cell. The inverse of the above matrix is:

$$\begin{bmatrix} 2/3 & 1/3 & 1/3 \\ -1/3 & 1/3 & 1/3 \\ -1/3 & -2/3 & 1/3 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_R &= 1/3\,(2h_H + k_H + \ell_H) \\ k_R &= 1/3\,(-h_H + k_H + \ell_H) \\ \ell_R &= 1/3\,(-h_H - 2k_H + \ell_H) \end{aligned}$$

Again a similar matrix can be found for the cubic-hexagonal transformation and is as follows:

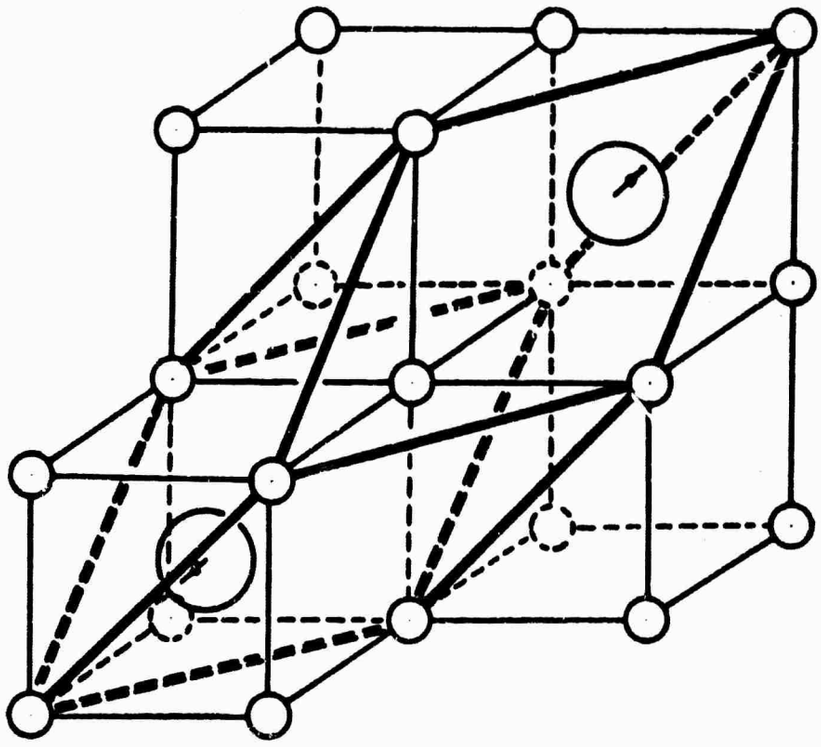
$$\begin{bmatrix} 0 & -1 & 1 \\ 1 & 0 & -1 \\ 2 & 2 & 2 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_H &= -k_C + \ell_C \\ k_H &= h_C - \ell_C \\ \ell_H &= 2(h_C + k_C + \ell_C) \end{aligned}$$

which is subject to the condition that the distortion is very slight. The inverse can be given as:

$$\begin{bmatrix} 1/3 & 2/3 & 1/6 \\ -2/3 & -1/3 & 1/6 \\ 1/3 & -1/3 & 1/6 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_C &= 1/6\,(2h_H + 4k_H + \ell_H) \\ k_C &= 1/6\,(-4h_H - 2k_H + \ell_H) \\ \ell_C &= 1/6\,(2h_H - 2k_H + \ell_H) \end{aligned}$$

FIGURE 1

CUBIC-RHOMBOHEDRAL UNIT CELLS



Small circles represent Al^{+3}

Large circles represent La^{+3}

The arrows show direction of La^{+3} shift

FIGURE 2

Growth Interface of Undoped Boule (Low Index)

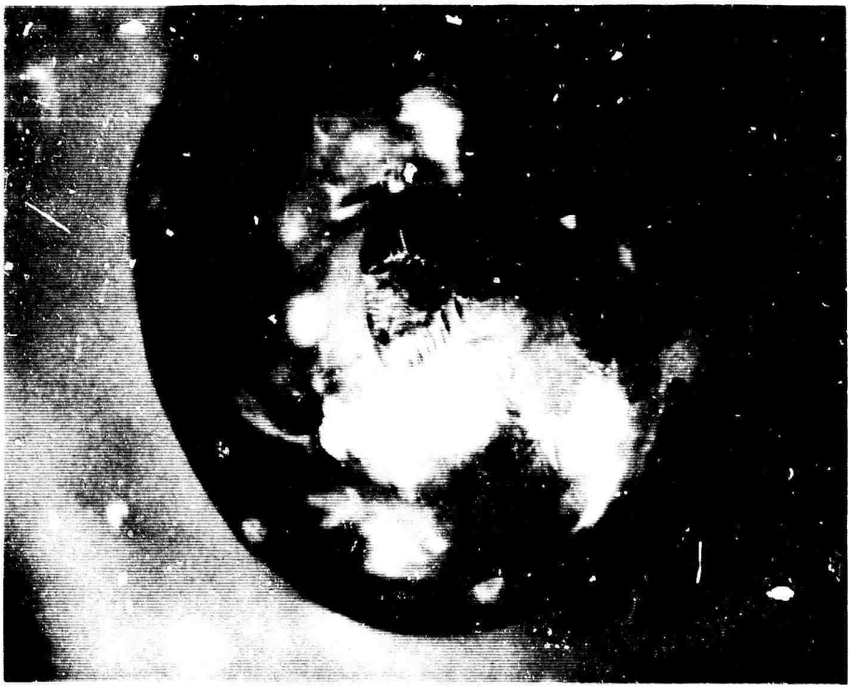


FIGURE 3

Growth Interface of Cr^{+3} Doped Boule (High Index)

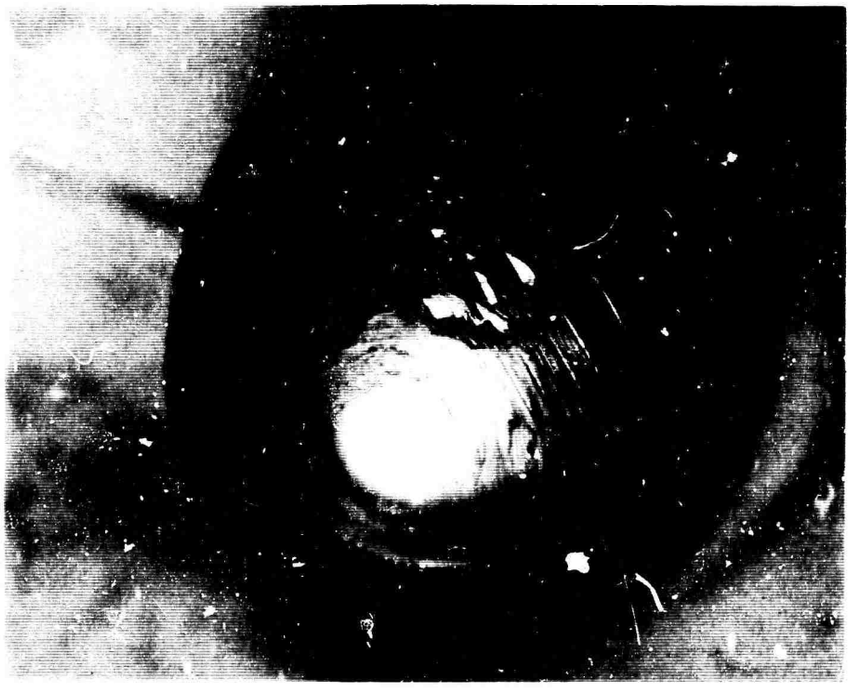


FIGURE 4

Effect of Pulling Rate on Lineage (IX)

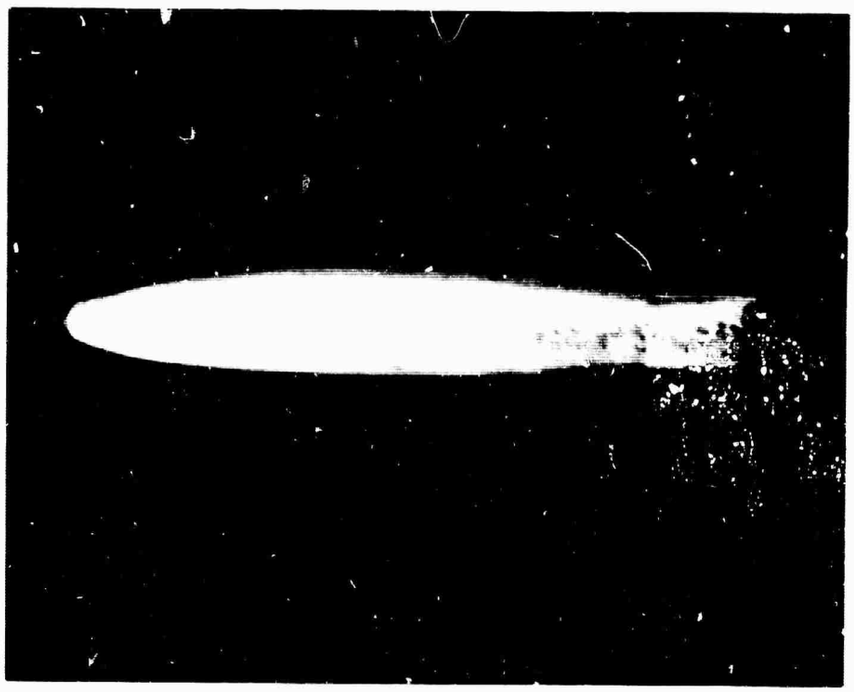
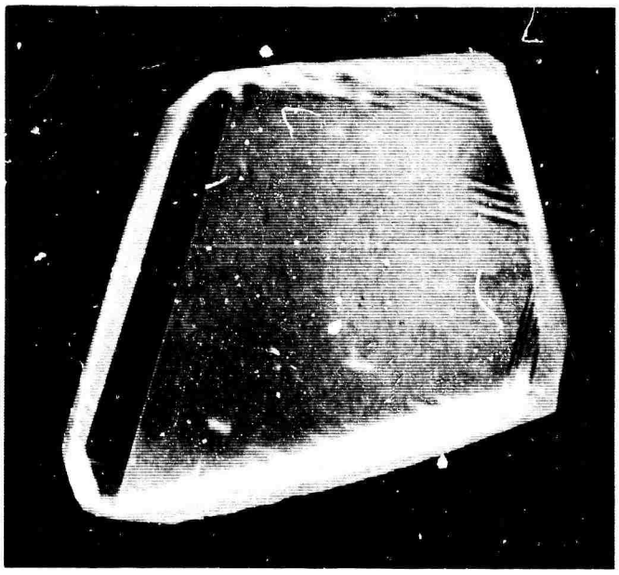


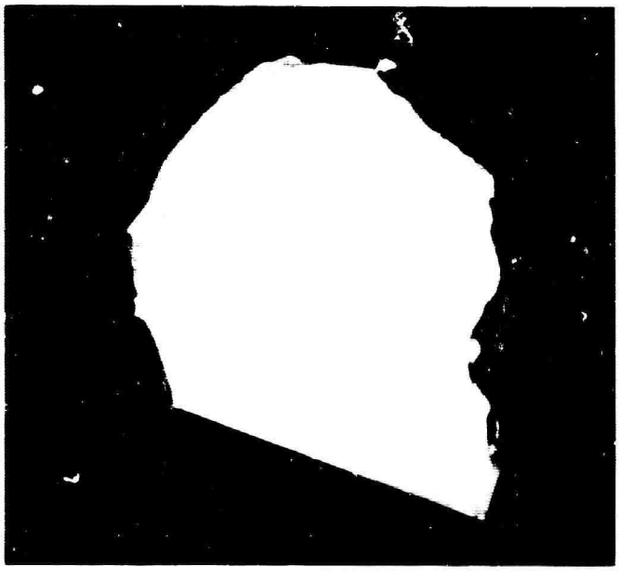
FIGURE 5

Twin Boundaries in Various Crystal Orientations



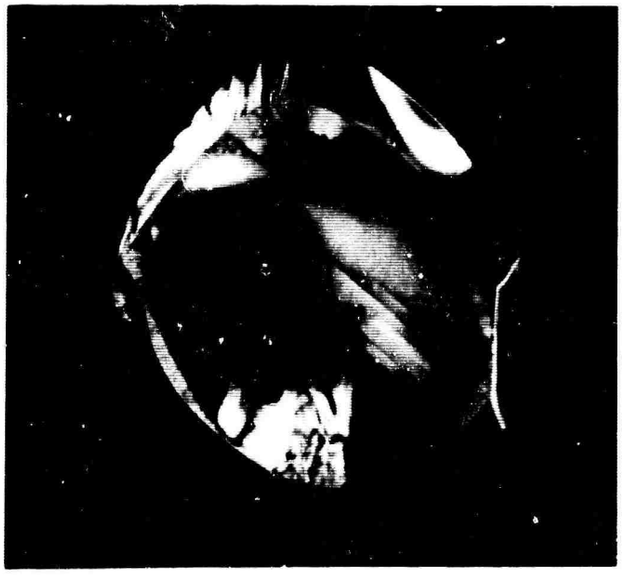
a

(110) Disk showing perpendicular and 45° twin boundaries. Approximately 7x



b

(100) Disk showing both sets of perpendicular twin boundaries. Approximately 7x

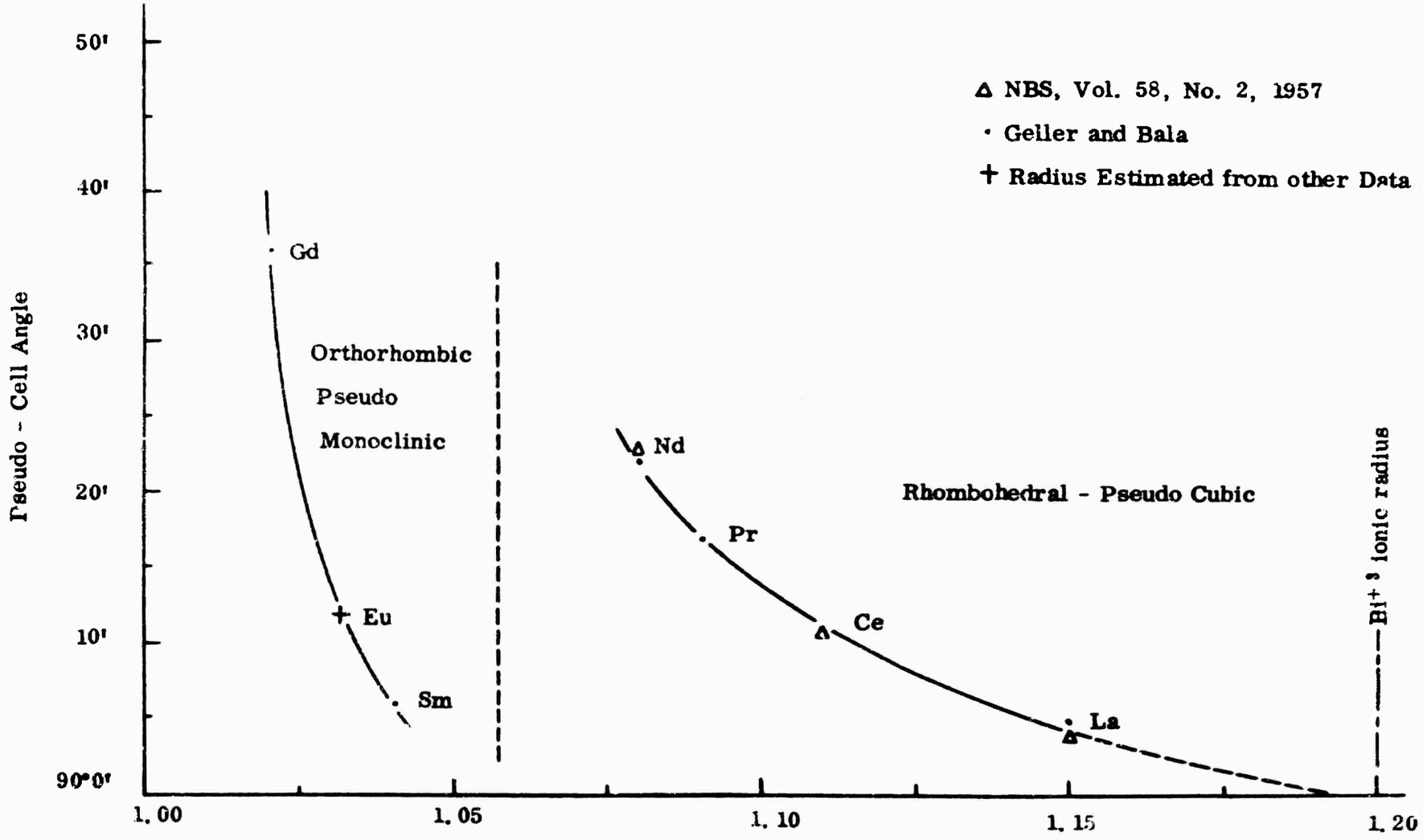


c

(111) Disk showing three sets of twin boundaries, each set 120° from the others. Approximately 7x

FIGURE 6

PSEUDO CELL ANGLE FOR RARE EARTH ALUMINATES



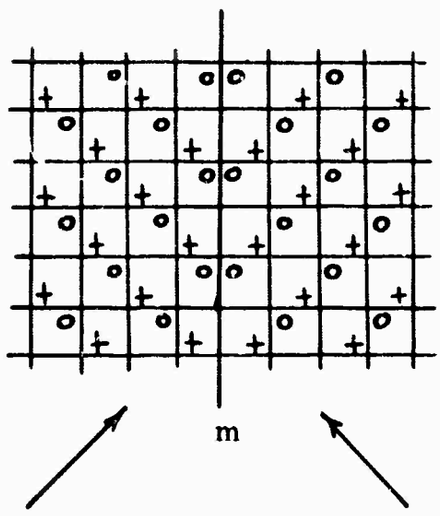
RARE EARTH IONIC RADIUS

FIGURE 7

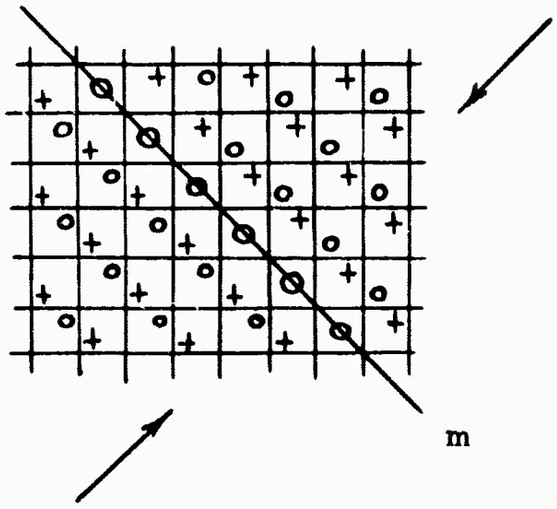
VARIOUS TYPES OF TWINNING

TRANSFORMATION TWINS

(100) Twin

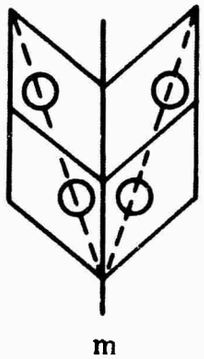


(110) Twin



GROWTH TWIN

(111) Twin



The grid on the first two figures represents the original cubic unit cell. The arrows represent the direction of the ⟨111⟩ axis. The circle (o) represents a shift of the La^{+3} ion in the direction indicated below the plane of the paper, the positive sign (+) a shift above the plane of the paper. The twin boundaries are represented by m (mirror planes). In the lower figure the large circle (O) represents the La^{+3} ion.

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13 ABSTRACT

The objective of this program was to explore the possibility of growing high optical quality $LaAlO_3$ by the Czochralski method. The techniques developed for ruby growth were found to be directly translatable to $LaAlO_3$ with no apparent limitations imposed by the use of a crucible. Undoped and doped (Cr^{3+}, Eu^{3+}) crystals of various orientations were grown.

Two major defects were encountered: color centers and twinning. Color centers were eliminated by using high purity starting materials in combination with selected growth and post-growth treatment. Two mechanisms for forming color centers are proposed and their relation to $LaAlO_3$ defect chemistry is discussed. The dominant twin planes have been identified to be those of the (100) system. Their relation to the crystal structure of $LaAlO_3$ has been elucidated.

Isolated attempts were made to grow $BiAlO_3$ and $PrAlO_3$ to determine if twinning might be a problem in these potential host compositions; other growth problems were encountered indicating that an answer could be obtained only by an extensive effort beyond the bounds of the present program.

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3	0853	ATTN TECHNICAL LIBRARY	54
4	0853	WATERTOWN, MASSACHUSETTS 02172	54
1	0875	BOULDER LABORATORIES	54
2	0875	NATIONAL BUREAU OF STANDARDS	54
3	0875	ATTN LIBRARY	54
4	0875	BOULDER, COLORADO	54
1	0918	AIR FORCE WEAPONS LABORATORY	54
2	0918	ATTN GUENTHER WLRPF	54
3	0918	KIRTLAND AIR FORCE BASE	54
4	0918	NEW MEXICO	54
1	0932	CHIEF, BUREAU OF NAVAL WEAPONS	54
2	0932	DEPARTMENT OF THE NAVY	54
3	0932	WASHINGTON 25, D. C.	54
4	0932	ATTN J. M. LEE RMGA-81	54
1	0976	AIR FORCE CAMBRIDGE RESEARCH LABORATORIES	54
2	0976	ATTN CRXL-R, RESEARCH LIBRARY	54
3	0976	LAWRENCE G. HANSCOM FIELD	54
4	0976	BEDFORD, MASSACHUSETTS	54
1	0988	BATTELLE MEMORIAL INSTITUTE	54
2	0988	505 KING AVENUE	54
3	0988	COLUMBUS 1, OHIO	54
4	0988	ATTN BMI-DEFENDER	54
1	1030	HEADQUARTERS, USAELRDL	54
2	1030	FORT MONMOUTH, NEW JERSEY 07703	54
3	1030	ATTN SELRA/SAR,NO-4, X, AND PF	54
1	1032	COMMANDER, U. S. NAVAL ORDNANCE TEST STATION	54
2	1032	CHINA LAKE, CALIF	54
3	1032	ATTN MR. G. A. WILKINS /CODE 4041/	54
1	1036	J. C. ALMASI	54 *
2	1036	GENERAL ELECTRIC COMPANY	54
3	1036	ADVANCED TECHNOLOGY LABORATORIES	54
4	1036	SCHENECTADY, N. Y.	54
1	1039	PROF. RUBIN BRAUNSTEIN	54 *
2	1039	UNIVERSITY OF CALIFORNIA	54
3	1039	DEPARTMENT OF PHYSICS	54
4	1039	LOS ANGELES 24, CAL.	54

1	1040	N. I. ADAMS	54 *
2	1040	PERKIN-ELMER CORP.	54
3	1040	NORWALK, CONN.	54
1	1046	E. P. REIDEL	54 *
2	1046	QUANTUM ELECTRONICS DEPT.	54
3	1046	WESTINGHOUSE ELECTRIC CORP.	54
4	1046	RESEARCH LABORATORIES	54
5	1046	PITTSBURGH, PA.	54
1	1047	PROF. H. G. HANSON	54 *
2	1047	UNIVERSITY OF MINNESOTA	54
3	1047	DULUTH, MINN	54
1	1048	P. SCHAFFER	54 *
2	1048	LEXINGTON LABORATORIES, INC.	54
3	1048	84 SHERMAN ST.	54
4	1048	CAMBRIDGE, MASS.	54
1	1049	L. E. RAUTIOLA	54 *
2	1049	LINDE COMPANY, DIVISION OF UNION CARBIDE	54
3	1049	EAST CHICAGO, IND.	54
1	1050	F. S. GALASSO	54 *
2	1050	UNITED AIRCRAFT CORP RESEARCH LABS.	54
3	1050	400 MAIN ST.	54
4	1050	EAST HARTFORD, CONN.	54
1	1051	J. W. NIELSON	54 *
2	1051	AIRTRON, DIVISION OF LITTON INDUSTRIES	54
3	1051	MORRIS PLAINS, N. J.	54
1	1052	E. M. FLANIGEN	54 *
2	1052	LINDE COMPANY	54
3	1052	DIVISION OF UNION CARBIDE	54
4	1052	TONAWANDA, N. Y.	54
1	1053	W. PRINDLE	54 *
2	1053	AMERICAN OPTICAL COMPANY	54
3	1053	14 MECHANIC ST.	54
4	1053	SOUTHBRIDGE, MASS.	54
1	1054	DR. ALAN HAUGHT	54 *
2	1054	PLASMA PHYSICS	54
3	1054	UNITED AIRCRAFT CORP.	54
4	1054	EAST HARTFORD 8, CONN.	54
1	1055	PROF. N. BLOEMBERGEN	54 *
2	1055	HARVARD UNIVERSITY	54
3	1055	DIVISION OF ENGINEERING & APPLIED PHYSICS	54
4	1055	CAMBRIDGE 38, MASS.	54

1	1056	PROF. R. J. COLLINS	54	*
2	1056	UNIVERSITY OF MINNESOTA	54	
3	1056	DEPARTMENT OF ELECTRICAL ENG.	54	
4	1056	MINNEAPOLIS 14, MINN.	54	
1	1057	DR. ALAN KOLB	54	*
2	1057	U. S. NAVAL RESEARCH LAB.	54	
3	1057	WASHINGTON, D. C.	54	
1	1058	PROF. J. M. FELDMAN	54	*
2	1058	CARNEGIE INSTITUTE OF TECHNOLOGY	54	
3	1058	DEPARTMENT OF ELECTRICAL ENGR.	54	
4	1058	PITTSBURGH 13, PENNA.	54	
1	1059	PROF. ARTHUR SCHAWLOW	54	*
2	1059	STANFORD UNIVERSITY	54	
3	1059	STANFORD, CALIFORNIA	54	
1	1060	J. ATWOOD	54	*
2	1060	ELECTRO-OPTICAL DIV.	54	
3	1060	PERKIN-ELMER CORP.	54	
4	1060	NORWALK, CONN.	54	
1	1065	RESEARCH MATERIALS INFORMATION CENTER	54	
2	1065	OAK RIDGE NATIONAL LABORATORY	54	
3	1065	POST OFFICE BOX X	54	
4	1065	OAK RIDGE, TENN. 37831	54	
5	1065	ATTN MR. T. F. CONNOLLY	54	
1	1066	J-5 PLANS AND POLICY DIRECTORATE	54	
2	1066	JOINT CHIEFS OF STAFF	54	
3	1066	REQUIREMENTS AND DEVELOPMENT DIVISION	54	
4	1066	ATTN SPECIAL PROJECTS BRANCH	54	
5	1066	ROOM 2D982, THE PENTAGON	54	
6	1066	WASHINGTON, D. C., 20301	54	
1	1067	ADVANCED RESEARCH PROJECTS AGENCY	54	
2	1067	RESEARCH AND DEVELOPEMENT FIELD UNIT	54	
3	1067	APO 143, BOX 41	54	
4	1067	SAN FRANCISCO, CALIF.	54	
1	1068	ADVANCED RESEARCH PROJECTS AGENCY	54	
2	1068	RESEARCH & DEVELOPMENT FIELD UNIT	54	
3	1068	APO 146, BOX 271	54	
4	1068	SAN FRANCISCO, CALIFORNIA	54	
5	1068	ATTN MR. TOM BRUNDAGE	54	
1	1082	AIR FORCE MATERIALS LABORATORY	54	*
2	1082	AIR FORCE SYSTEMS COMMAND	54	
3	1082	WRIGHT-PATTERSON AIR FORCE BASE, OHIO	54	
4	1082	ATTN MAAM /LT. JOHN H. ESTESS/	54	

1	1083	DR. C. H. CHURCH	54 *
2	1083	WESTINGHOUSE ELECTRIC CORPORATION	54
3	1083	RESEARCH LABORATORIES	54
4	1083	PITTSBURGH 35, PENNA.	54
1	1084	PROF. DONALD S. MCCLURE	54 *
2	1084	INSTITUTE FOR THE STUDY OF METALS	54
3	1084	UNIVERSITY OF CHICAGO	54
4	1084	CHICAGO 37, ILLINOIS	54
1	1085	DR. DANIEL GRAFSTEIN	54 *
2	1085	GENERAL PRECISION, INC.	54
3	1085	AEROSPACE GROUP	54
4	1085	LITTLE FALLS, NEW JERSEY	54
1	1087	DR. R. C. LINARES	54 *
2	1087	PERKIN-ELMER CORPORATION	54
3	1087	SOLID STATE MATERIALS BRANCH	54
4	1087	NORWALK, CONN.	54
1	1088	DR. R. C. OHLMANN	54 *
2	1088	WESTINGHOUSE RESEARCH LABORATORIES	54
3	1088	PITTSBURGH 35, PENNA.	54
1	1089	PROFESSOR S. CLAESSON	54 *
2	1089	UPPSALA UNIVERSITY	54
3	1089	UPPSALA, SWEDEN	54
1	1136	COMMANDING OFFICER	54
2	1136	OFFICE OF NAVAL RESEARCH BRANCH OFFICE	54
3	1136	BOX 39, FPO	54
4	1136	NEW YORK, NEW YORK 09510	54
1	1122	DR. C. B. ELLIS	54 *
2	1122	GPL DIVISION	54
3	1122	GENERAL PRECISION, INC.	54
4	1122	63 BEDFORD ROAD	54
5	1122	PLEASANTVILLE, NEW YORK	54
1	1172	MR. C. M. STICKLEY	54
2	1172	AIR FORCE CAMBRIDGE RESEARCH	54
3	1172	LABORATORIES - CROL	54
4	1172	LAURENCE G. HANSCOM FIELD	54
5	1172	BEDFORD, MASSACHUSETTS 017[illegible]	54
1	1177	DR. WAYNE H. KEEN	54 *
2	1177	WESTINGHOUSE DEFENSE & SPACE CENTER	54
3	1177	/SURFACE DIVISION/	54
4	1177	P. O. BOX 1897	54
5	1177	BALTIMORE, MARYLAND 21203	54

1	1178	DR. C. J. KOESTER	54 *
2	1178	AMERICAN OPTICAL COMPANY	54
3	1178	RESEARCH CENTER	54
4	1178	SOUTHBRIDGE, MASSACHUSETTS	54
1	1179	DR. RAY HOSKINS	54 *
2	1179	KORAD CORPORATION	54
3	1179	3520 COLORADO AVENUE	54
4	1179	SANTA MONICO, CALIFORNIA 90406	54
1	1180	DR. J. W. CARSON	54 *
2	1180	HUGHES AIRCRAFT COMPANY	54
3	1180	CULVER CITY, CALIFORNIA	54
1	1181	DR. MARVIN LASSER	54 *
2	1181	PHILCO CORPORATION	54
3	1181	RESEARCH LABORATORIES	54
4	1181	BLUE BELL, PENN.	54
1	1183	PROF. A. SMAKULA	54 *
2	1183	CRYSTAL PHYSICS LAB	54
3	1183	MASSACHUSETTS INSTITUTE OF TECHNOLOGY	54
4	1183	CAMBRIDGE, MASS	54
1	1184	DR. F. MCCLUNG	54 *
2	1184	HUGHES RESEARCH LABORATORIES	54
3	1184	3011 MALIBU CANYON ROAD	54
4	1184	MALIBU, CALIFORNIA 90265	54
1	1185	DR. M. C. TOBIN	54 *
2	1185	PERKIN-ELMER CORPORATION	54
3	1185	NORWALK, CONNECTICUT	54
1	1186	PROF. G. W. STROKE	54 *
2	1186	ELECT. ENGINEERING DEPT.	54
3	1186	THE UNIVERSITY OF MICHIGAN	54
4	1186	ANN ARBOR, MICHIGAN 48107	54

FURTHER ADDITIONS TO LIST 54*

Robert L. Parker
National Bureau of Standards
Washington, D.C.

N.D. Schoenberger
Precision Instrument Company
3170 Porter Drive
Palo Alto, California

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*Authorized by letter

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NR 017-708
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